Synthesis and Characterization of Ag doped ZnO-PVP Composite Nanofibers by Electrospinning Method

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CERTIFICATE

*This is to certify that the dissertation entitled "**Synthesis and Characterization of Ag doped ZnO-PVP Composite Nanofibers by Electrospinning Method"** by Shraban Kumar Sahoo (Roll No.: 412CY2021) tothe department of chemistry, National Institute of Technology,Rourkela for the degree of Master of Science in Chemistry is based onthe result obtained in the bonafide project work carried out by himunder my guidance and supervision.*

I further certify that to the best of my knowledge Shraban Kumar Sahoobears a good moral character.

Supervisor

Place: Rourkela
Date:

Dr. GarudadhwajHota,

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Rourkela-769008

DECLARATION

IShraban Kumar Sahoohereby declare that this project report entitled "***Synthesis and characterization of Ag doped PVP-ZnO composite nanofiber by Electrospinning Techniques*****"** is the original workcarried out by us under supervision of **Dr.GarudadhwajHota**, Department of chemistry, National Institute ofTechnology Rourkela (NIT), Rourkela and the present work or any other part thereof has not been presented to any other University or Institution for the award of any other degree regardingto our belief

Shraban Kumar Sahoo

Roll No.: 412CY2021

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Shraban Kumar Sahoo

ABSTRACT

One-dimensional (1D) nanomaterials such as nanowires, nanotubes, nanorods, nanofibers and nanobelts have drawn a lot of attention arising out oftheir unique optical, magnetic, electrical, and otheremerging properties. Among them nanofibers provide several amazing characteristics such as very large surface area to volume ratio, high porosity, high gas permeability, small interfibrous pore size, flexibility in surface functionalities. A number of methods have been used to fabricate nanofibers but electrospinning only method to be the simplest, costeffective and highly versatile technique that has been widely used for the fabrication continuous fibers. In the present work we have synthesized ZnO-PVP composite nanofiber and Ag doped ZnO-PVP composite nanofibers by electrospinning method. The formation, crystalline phase and morphology of the prepared nanofibers were analysed by FT-IR spectroscopy, XRD andFE-SEM analytical techniques. Formation of ultra-fine continuous smooth fibers with diameter in the range of 150-450 nm and length up to several microns was observed in case of ZnO-PVP composite nanofiber. However, in case of Ag doped ZnO-PVP composite nanofibers, no significant change in fibers diameter was observed.The magnified SEM images indicate the formation of around 20-50 nm spherical Ag particles on the surface of the nanofiber. The formation of ZnO in composite nanofiber was confirmed by XRD analysis. Furthermore, additional peaks of Ag_3O_4phase was observed in the XRD pattern of Ag doped ZnO-PVP composite nanofiber.

Key words: 1D-Nanomaterials, Nanofiber, Electrospinning, Functionalization, Doping.

1. Introduction

Nanoscience is the study of nanoscale materials that exhibit remarkable properties, functionality and phenomena due to the influence of small dimensions [1]. Nanomaterials are materials having at least one dimension less than 100 nm. Nanotechnology is the manipulation of matter at an atomic and molecular scale which deals with materials, devices, and other structures with at least one dimension sized from 1 to 100 nm. Arising out of their size and surface dominated properties nanomaterials exhibit unique optical, magnetic, electrical, and other emerging properties. Due to these important properties nanomaterials having wide range of applications in the field of electronics, fuel cells, batteries, agriculture, food industry, and medicines, etc [2]. Nanofibers are important 1D nanomaterial that provides several amazing properties such as very large surface area to volume ratio, high porosity, high gas permeability, small interfibrous pore size, flexibility in surface functionalities [3, 4]. Due to these outstanding properties nanofibers are used in many important applications, such as biomedical [5], electrical and optical [6], protective clothing [7], filtration [8], antibacterial activity [9] etc.

A number of methods have been used to fabricate nanofibers. Among the different methods, electrospinning seems to be the simplest, low cost and highly versatile technique that allows for the fabrication continuous fibers with diameters ranging from a few nanometers to micrometers. In electrospinning method, a high voltage is applied to a polymer solution to induce an electrified jet on the tip of a metallic needle that lads to form the nanofibers on the surface of a metallic collector followed by evaporation of solvents [10, 11].

Recent research focussed on the surface functionalization of nanofibers specifically impregnation of nanoparticles on the surface of the fibers to improve the perfermance. Jin et al., [12] have studied the synthesis of Poly(N-vinylpyrrolidone) (PVP) nanofibers containing Ag nanoparticles electrospinning the PVP nanofibers containing $AgNO_3$. They have used N, N- Dimethylformamide (DMF) as solvent for the PVP as well as reducing agent for the synthesis of Ag nanoparticles. The average size of the Ag nanoparticles was found to be 4.5 nm.

1.2. Objective of the work

- To prepare PVP-Zn$(CH_3COO)_2$ nanofibers by electrospinning technique.
- To prepare Ag doped $(CH_3COO)_2$ Zn-PVP nanofiber by electrospinning technique.
- In situ growth of ZnO and Ag nanoparticles on the surface of PVP nanofibers by heat treatment
- Characterization of ZnO-PVP and Ag doped ZnO-PVP nanocomposite fibers by FTIR, XRD, UV-visible and FE-SEM analytical techniques.

2. Experimental Section

2.1. Materials and methods

Polyvinylpyrrolidone (PVP) was purchased from Sigma Aldrich (US). Zinc acetate ($(CH_3COO)_2Zn$), Silver nitrate ($AgNO_3$), and Ethyl alcohol (C_2H_5OH), were purchased from Merck (INDIA). All chemicals were used without further purifications and 25 ml neat cleaned glass bottle with few screw capped. Double distilled water have been used in throughout the experiment.

2.2. Synthesis of Electrospun ZnO-PVP composite nanofibers

Prior to electrospinning, we have prepared the PVP solution by dissolving required amount of PVP in ethyl alcohol. Separately we have also prepared Zinc acetate solution was required amount of PVP by dissolving it in ethyl alcohol. Then mechanical stirring was performed for 1 h for complete solubility of both the solution. Then the two solutions were mixed and again mechanical stirring was applied for 4-5 h to prepare homogeneous electrospinning solution. Then the resulted PVP-zinc acetate electrospinning solution was taken in a plastic syringe fitted with a metallic needle and the syringe was fixed by a syringe pump. On applying electric field to the electrospinning solution, jets like fine fibers are formed followed by evaporation of solvent. Then PVP- zinc acetate nanocomposite fibers membrane was collected from the metallic collector. In order to prepare PVP-ZnO nanocomposite fibers, the obtained nanocomposite fibers are put in a muffle furnace at 200 ˚C for 4 hours.

2.3. Synthesis of Ag/ZnO functionalized PVP nanofibers

Homogeneous solution of PVP-zinc acetate was prepared using the same procedure as described above. To the above prepared solution, different mass percent of $AgNO_3$ was dissolved separately and continued mechanical stirring for 12 h to obtain homogeneous electrospinning solution. The same condition was applied for the electrospinning of PVP-zinc acetate-silver nitrate solution as described above. Then the obtained electrospun nanofibers membrane was put in the muffle furnace at 200 ˚C for 4 h to prepare Ag doped PVP-ZnO nanocomposite fibers.

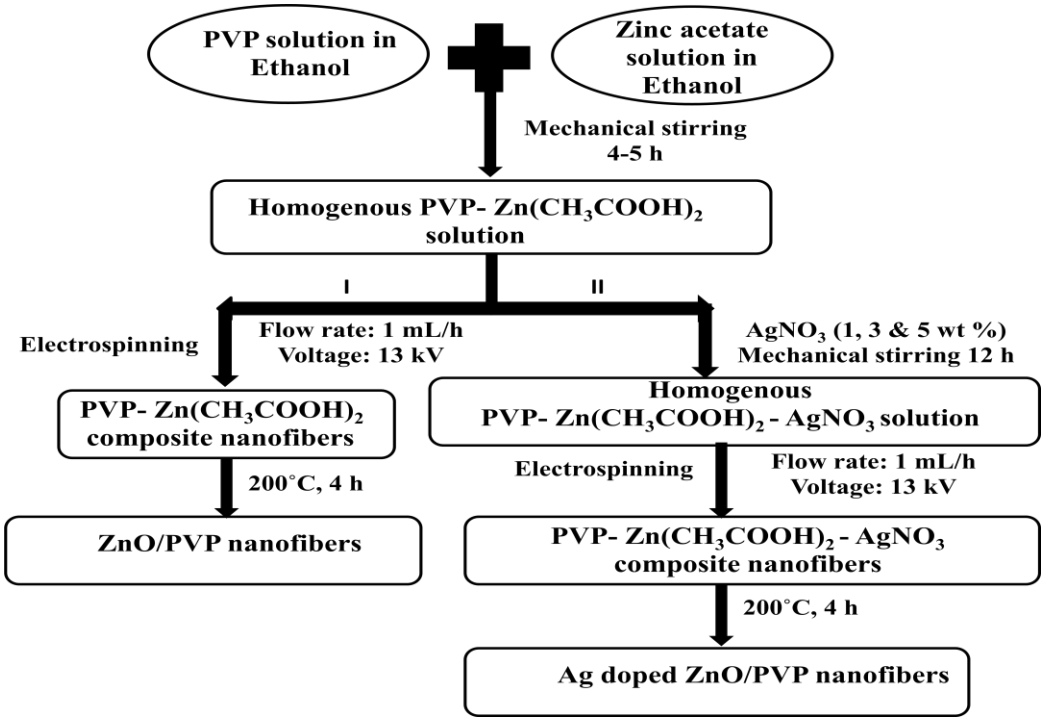

Figure 2.1 Flow chart for the synthesis of Electrospun ZnO-PVP composite nanofibers and Ag/ZnO functionalized PVP nanofibers.

3. Results and discussion

3.1 Characterization of ZnO-PVP nanofibers

3.1.1 FTIR Analysis

Fourier transform infrared spectroscopy (FTIR) results were recorded using Perkin-Elmer FTIR (Spectrum RX-I) spectrophotometer. The spectra of PVP-ZnO composite nanofiber and Ag doped PVP-ZnO composite nanofibers were taken in the spectral range of 4000-400 cm^{-1}

and the patterns are presented in figure 3.1. Figure 3.1 (a) is the IR spectra of PVP-ZnO composite nanofiber and figure 3.1 (b), (c) and (d) are the IR spectra of 1%, 3% and 5% Ag doped PVP-ZnO composite nanofibers, respectively. From the figure, the peak around 3442 $cm^{-1}$is due to O-H stretching vibration, indicating the presence of water crystallisation in the prepared samples. The peaks at 2930 and 1658 $cm^{-1}$are due to the unsymmetrical stretching vibration of methylene (-CH_2-) group and symmetrical stretching of carbonyl group (-C=O), respectively. The peaks at 1425 and 1272 $cm^{-1}$are due to bending vibration of methylene (CH_2-) group and stretching vibration of nitrile group (-CN-), respectively. Again,the peak at 470 cm^{-1} corresponds to the Zn–O. This may be due to PVP capping of ZnO nanoparticle in the prepared nanofiber [13].

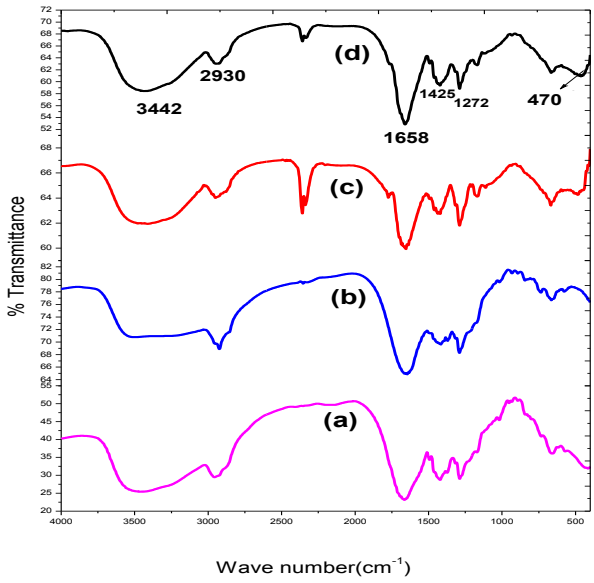

Figure 3.1 FT-IR spectra of (a) ZnO-PVP composite nanofiber, (b) 1%Ag doped ZnO-PVP composite nanofibers, (c) 3% Ag doped ZnO-PVP composite nanofibers and (d) 5% Ag doped ZnO-PVP composite nanofibers.

3.1.2 FE-SEM analysis

In order to study the surface morphology of ZnO-PVP composite nanofibers, we have preformed FE-SEM analysis. The FE-SEM image of prepared ZnO–PVP composite electrospun nanofiber along with the EDAX spectrum is illustrated in figure 3.2. The micrographs in figure 3.2 suggest the formation of ultra-fine continuous smooth fibers with

diameter around 150-450 nm and length of to several micrometer. The surfaces of the composite nanofibers very smooth without any defect. From EDAX spectrum, the detected peaks of C, Zn and O indicate that Fictionalization the ZnO on the PVP fibers surface.

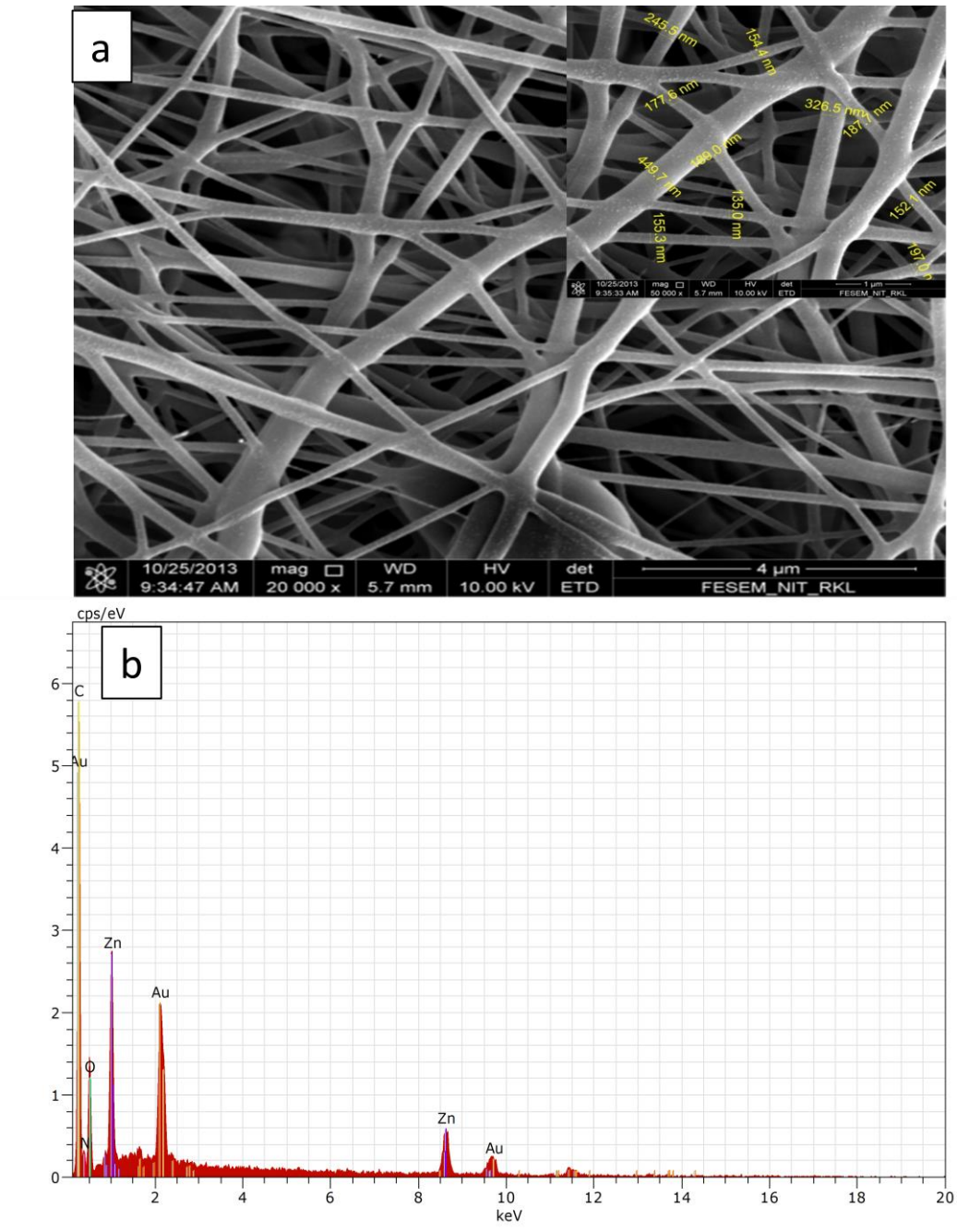

Figure 3.2 (a) FE-SEM images and (b) EDAX Spectra of ZnO–PVP composite nanofiber.

Similarly the morphologies of Ag doped ZnO–PVP composite electrospun nanofibers along with the EDAX spectrum are illustrated in figure 3.3. It is observed that, the Ag doped ZnO–PVP nanofibers contain the same morphology of parent ZnO–PVP nanofiber and there is no appraisable change in fiber diameter is observed. The surface of the nanofibers are not smooth due to presence of very fine Ag nanoparticles with particle diameters around 10-50 nm on the fiber surfaces.The EDS spectrums of the Ag doped PVP-ZnO nanofibers showed the presence of C, Zn, and O along with Ag peaks and the Intensity of Ag peaks increase with increasing percentage of doping.

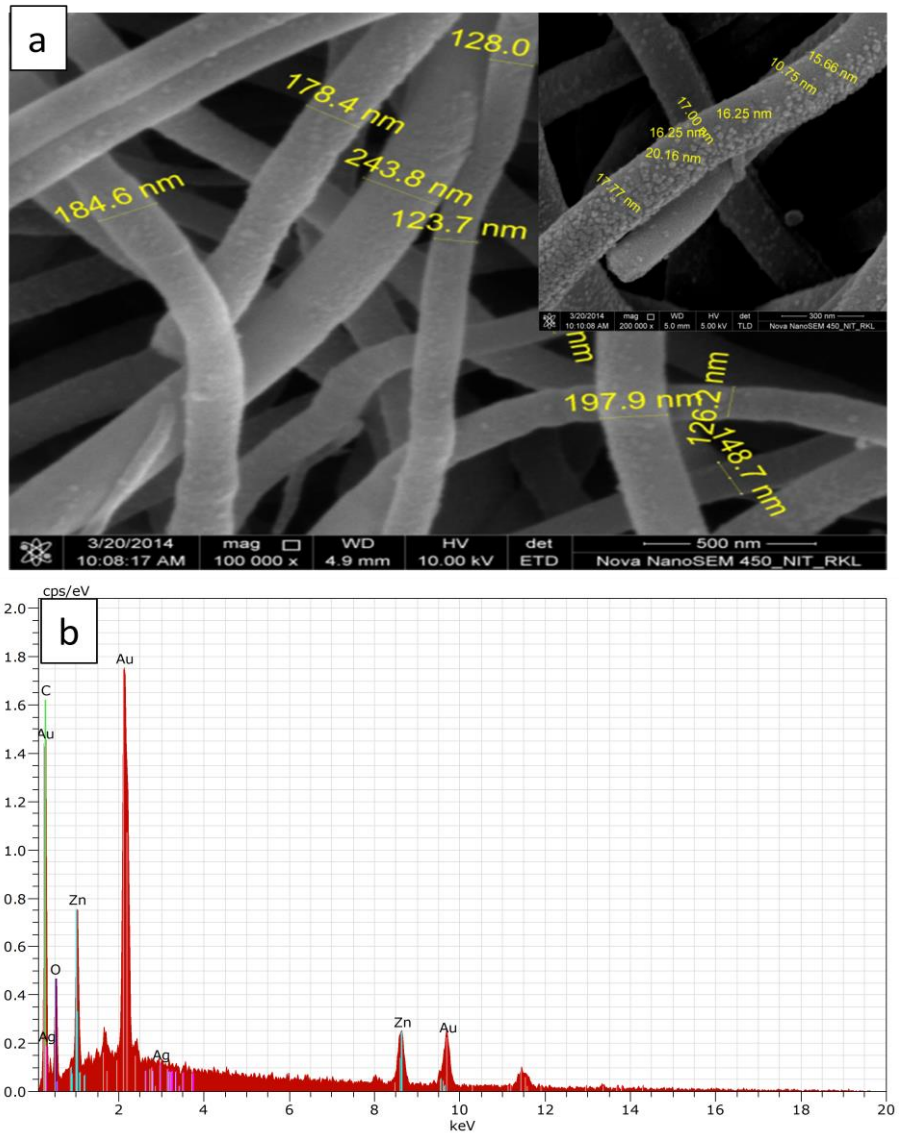

Figure 3.3 (a) FE-SEM images and (b) EDAX Spectra of 1 % Ag doped PVP-ZnO composite nanofibers.

3.1.3 X-ray diffraction analysis

The formation and phase analysis of the prepared nanofibers were analysed by Rigaku Ultima-IV X-ray diffractometer with Cu Kα radiation (λ = 1.5418 Å). Figure 3.4 shows the XRD patterns of PVP/ZnO and Ag doped Composite nanofibers. All the patterns contain a broad peak each around 2θ=21.2°, corresponding to the peak of PVP crystalline. Figure 3.4 (a), (b), (c) and (d) patterns contain peaks at 31.73°, 34.21°, 36.15°, 47.35°, 56.62°, 62.74° and 67.84°. These peaks are corresponding to hexagonal ZnOcrystal system according to JCPDS card number 79-0206. Along with the peaks of PVP and ZnO, the Ag doped composite fibers contains some additional peaks at 33.1°, 38.25°, 44.32°, 59.1°, 64.34° and 66.14°. These peaks are due to presence of monoclinic Ag_3O_4 crystal system according JCPDS card number: 40-1054. This observation indicates the formation of Ag_3O_4in the PVP/ZnO composite nanofiber matrix due to Ag doping. The Ag_3O_4 peaks are more pronounced in case of 3 % and 5% Ag doped PVP/ZnO composite nanofiber system.

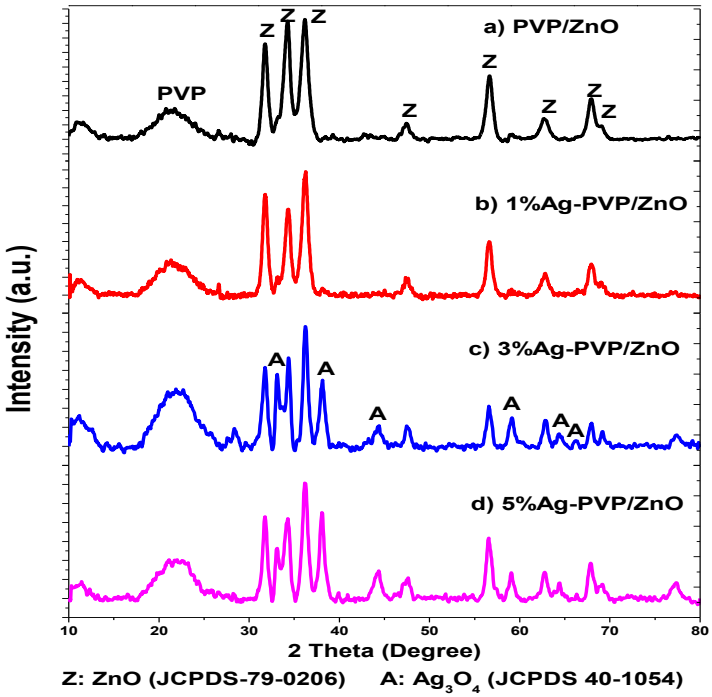

Figure 3.4 XRD patterns of a) PVP-ZnO, b) 1% Ag doped ZnO-PVP, c) 3% Ag doped ZnO-PVP, and d) 5% Ag doped ZnO-PVP composite nanofibers.

4. Conclusions and future works

4.1 Conclusion

ZnO-PVP composite nanofiber along with 1%, 3% and 5% Ag doped ZnO-PVP composite nanofibers have been synthesized successfully by electrospinning method. The formation, crystallise phage and morphology of the prepared nanofibers were analysed by FT-IR spectroscopy, XRD and FESEM analytical techniques. Formation of ultra-fine continuous smooth fibers with diameter in the range of 150-450 nm and length of to several microns was observed in case of ZnO-PVP composite nanofiber. In case of Ag doped ZnO-PVP composite nanofiber comparative diameter were observed along with very small nanoparticles with diameter around 20-50 nm on the surface of the nanofiber. The formation of ZnO in composite nanofiber was confirmed by XRD analysis. Again the Ag doped system contains peaks of Ag_3O_4 nanoparticles along with PVP and ZnO in the Ag doped composite nanofiber system.

4.2 Scope of future works

- Antibacterial activity study of ZnO-PVP composite nanofibers and Ag doped ZnO-PVP composite nanofibers.
- Environmental applications of the above prepared nanofibers towards the adsorption and photocatalytic degradation of toxic organic dyes from aqueous system, need to be carried out.

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